



Synthesis of CdS-decorated MIL-68(Fe) nanocomposites: Efficient and stable visible light photocatalysts for the selective reduction of 4-nitroaniline to *p*-phenylenediamine in water



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ABSTRACT

Visible-light-initiated organic transformations have received much attention because of low cost, relative safety, and environmental friendliness. In this work, a series of CdS-decorated MIL-68(Fe) nanocomposites (CdS-M68 NCs) have been prepared via a facile room-temperature photodeposition technique in a controlled manner. Importantly, the CdS-M68 NCs exhibit remarkably enhanced photoactivity toward selective reduction of 4-nitroaniline (4-NA) to *p*-phenylenediamine (PPD) in water under visible light irradiation ($\lambda \geq 420$ nm) as compared to bare CdS and MIL-68(Fe), giving a 4-NA conversion of $\sim 100\%$ after irradiation for 8 min. The significantly enhanced photoactivity is attributed to the integrated factors of the effective transportation of the photogenerated electron-hole pairs and the enhanced visible light absorption intensity. Combining with trapping experiments and ESR analysis, it could be revealed that the photoexcited electrons and $\cdot\text{CO}_2^-$ radicals should be the main active species in the present system. In addition, a possible photocatalytic reduction mechanism has been investigated.

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1. Introduction

Aminobenzenes are an important class of industrial intermediates for a variety of industrial chemicals. *p*-phenylenediamine (PPD), as a member of the aminobenzenes, is a useful ingredient to many industrial chemicals (e.g., rubber antioxidants, textile fibers and thermoplastics) [1–3]. In the past, direct catalytic hydrogenation of 4-nitroaniline (4-NA) has been proved to be an effective process for the preparation of PPD [1]. However, this process suffers from the limitations of rigorous reaction conditions, high costs and tedious procedures. Therefore, developing general, economic and simple routes for the preparation of PPD is required. Recently, various methods, such as electrochemical systems and photocatalysis, have been reported for the preparation of aminobenzenes [4–6]. Among these methods, visible-light photocatalysis has emerged as a powerful technique since it achieves the one-pot preparation of aminobenzenes by reducing nitrobenzenes in water under sunlight irradiation.

Up to now, numerous photocatalysts have been discovered for this reaction. Cadmium sulfide (CdS) is one of the most promising materials, which has been studied widely due to its visible light response and appropriate position of conduction band. Nevertheless, the fast recombination of photogenerated electron-hole pairs and the lack of catalytic sites are two key factors that hinder the enhancement of photocatalytic performance of pure CdS [7]. Many attempts have been made to enhance the activity of CdS, such as nanostructuring and coupling with other materials. Actually, combining CdS with other semiconductors to construct heterostructures (e.g. CdS-SnO₂, CdS-TiO₂, CdS-C₃N₄) is considered as one of the best approaches to suppress the recombination of photogenerated charge carriers [8–11]. However, the common CdS-semiconductor hybrids often suffered from the drawbacks of poor interface contact, low specific surface area, lack of catalytic sites and reaction centers. Thus, there is still plenty of room to explore unfulfilled potentials for improving the fabrication and properties of CdS-based photocatalysts.

Metal-organic frameworks (MOFs) are a class of crystalline materials formed by transition metal-containing clusters as structural nodes bridged by organic linkers. [12]. As the historic work made by García et al. on UV light induced phenol photodegradation using MOF-5 as a semiconductor in 2006, a range of photoactive

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MOFs have been discussed by researchers with great enthusiasm [13–17]. In our previous study, we have also shown that the MIL-68(Fe) could serve as a type of efficient photocatalysts for photocatalytic reduction reaction driven by visible light irradiation [18]. Compared with traditional semiconductor photocatalysts, the superiority of the photosensitive MOFs as supporters for CdS lie in the fact that (i) ultrahigh surface area can be expected on such hybrid materials; (ii) the narrow micropore distribution may lead to the formation of monodisperse CdS particles. More importantly, it could be expected that a photoactive MOF can not only serve as a host to control the encapsulation of CdS, but also facilitate the separation of photogenerated charge carriers by forming the effective interfacial contact with CdS when the two components have well-matched band structures [19,20]. Although there have been some reports on semiconductor-MOFs nanocomposites (NCs) [21–23], it should be noted that the reports on CdS-MOFs NCs for photocatalytic applications are rather scarce. Especially, the unique CdS-MOFs NCs into photocatalytic selective reduction of nitro organics under visible light, to the best of our knowledge, have not been thoroughly investigated.

Herein, we report for the first time the synthesis of CdS-decorated MIL-68(Fe) via a facile photodeposition method. MIL-68(Fe), which consists of chains of corner-sharing Fe-O octahedra connected through 1,4-benzenedicarboxylic acid linker, possesses with high stability [18,24]. Moreover, its photocatalytic makes it as an intriguing candidate for our study. The as-synthesized CdS-MIL-68(Fe) (denoted as CdS-M68) NCs have exhibited remarkably enhanced visible light photoactivities toward selective reduction of nitro organic as compared to the original MIL-68(Fe) and CdS. The origin accounting for the improved photoactivity and the underlying reaction mechanism have been studied in terms of a series of characterizations and controlled experiments using radical scavengers. Finally, a possible reaction mechanism of photocatalytic reduction of 4-NA to PPD in solutions through CdS-M68 NCs have also been investigated in detail. It is expected that our current research could provide a new way to design MOF-semiconductor photocatalysts and their applications as visible light photocatalysts toward selective organic transformations.

2. Experimental

2.1. Materials and reagents

Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was supplied by Aladdin Reagent Co., Ltd. 1,4-benzenedicarboxylic acid (H_2BDC) was obtained from Alfa Aesar China Co., Ltd., cadmium chloride ($\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$), elemental sulfur (S_8), hydrofluoric acid (HF, 49%), hydrochloric acid (HCl), N,N-Dimethylformamide (DMF), acetone, ethanol and ammonium formate (HCO_2NH_4) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All materials were used as received without further purification.

2.2. Synthesis of MIL-68(Fe) samples

MIL-68(Fe) was obtained according to the strategy that reported in previous [18]. A mount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and H_2BDC (molar ratio = 1:2) were mixed with 12 mL DMF in a Teflon-lined autoclave, then 120 μL HF (5 mmol) and 120 μL HCl (1 mmol) were added, followed stirring for another 30 min to blend completely. After that, the Teflon-lined was heated at 100 °C for 120 h. The products were left cool at room temperature, collected by centrifugation and washed with deionized water and acetone several times to eliminate the DMF molecules in the pores. Finally, the recovered solid was dried at 100 °C vacuum oven for 24 h.

2.3. Fabrication of CdS-MIL-68(Fe) NCs

The CdS-MIL-68(Fe) NCs were synthesized by a photodeposition method. First, a certain amount of the MIL-68(Fe) was evenly dispersed in 25 mL of absolute ethanol. Then, we added 10 mg of S_8 and 78 mg of $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ and bubbled with nitrogen for 30 min in the dark. Last, the suspension was irradiated with a 300 W Xe arc lamp with incident light at $\lambda \geq 420$ nm for 2, 4, or 6 h. The obtained samples were labeled as X-CdS-M68, where X = 2, 4 and 6 according to the photodeposition time.

2.4. Characterizations

The X-ray diffraction (XRD) patterns of the samples were carried on a Bruker D8 Advance X-ray diffractometer operated at 40 kV and 40 mA with Ni-filtered Cu K α irradiation. The data were recorded in the 2 θ ranging from 3° to 70° with a step width of 0.05°. The Brunauer-Emmett-Teller (BET) surface area was measured with an ASAP2020 M apparatus (Micromeritics Instrument Corp., USA). Before the test, the samples were degassed in vacuum at 120 °C for 6 h. The nitrogen adsorption and desorption isotherms were measured at 77 K. UV-vis diffuse reflectance spectra (UV-vis DRS) were obtained by a Cary 500 UV-vis-NIR spectrophotometer in which BaSO_4 powder was used as the internal standard to obtain the optical properties of the samples over a wavelength range of 330–650 nm. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a PHI Quantum 2000 XPS system equipped with a monochromatic Al K α X-ray source to obtain the surface elemental composition of the sample. The Mott-Schottky analysis was performed at a Zenuium electrochemical workstation. The electrochemical measurements were performed in a conventional three electrode cell, Ag/AgCl electrode was used as the reference electrode and a Pt plate was used as the counter electrode. The photocurrent measurements were conducted with a BAS Epsilon workstation. The Mott-Schottky experiments were conducted on a Precision PARC workstation. Electron spin resonance (ESR) signals of spin-trapped paramagnetic species with 5,5-dimethyl-1-pyrrolineN-oxide (DMPO) were recorded with a Bruker A300 spectrometer. A 300 W Xe lamp (Beijing Perfectlight, PLS-SXE300c) with a 420 nm cut-off filter was used as a light source.

2.5. Evaluation of photocatalytic activity

For the photocatalytic reduction of 4-nitroaniline (4-NA) and *p*-phenylenediamine (PPD), an ozone-free 300 W Xe lamp (PLS-SXE300C, Trusttech Co. Ltd, Beijing) with a cut off filter of 420 nm and an infrared filter was used as the light source ($\lambda \geq 420$ nm). Prior to the catalytic test, 40 mg of photocatalyst was suspended in 40 mL of 4-NA (A.R., Alfa Aesar Co.) aqueous solution (20 mg/L) in a glass reactor (100 mL). Nitrogen was then purged through the system, followed by the introduction of 20 mg of HCO_2NH_4 . After that, the suspension was stirred in the dark for 1 h to ensure the establishment of adsorption-desorption equilibrium between the sample and 4-NA. As the reaction proceeded, 3 mL of the suspension was taken at a certain interval and was centrifuged (12000 rpm, 2 min). The 4-NA and PPD concentrations during the reaction were analyzed by measuring the absorbance at 380 and 238 nm with a Cary 50 UV-vis spectrophotometer (Varian Co.), respectively. The reactant and product identification were also confirmed by the high performance liquid chromatography (HPLC, Agilent 1260). Separation was carried out at about 23 °C on the Xtimate™ C18 column (4.6 mm \times 150 mm, 5.0 μm particle size). The mobile phase consisted of H_2O -acetonitrile solution (75:25, v/v), at a flow rate of 0.8 mL/min, the wavelength for detection was adjusted to 228 nm.

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